Studies of Chloranil–Donor Adducts by X-Ray Photoelectron Spectroscopy (ESCA)

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Abstract: Adducts of chloranil with hexamethylbenzene (HMB), *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), triphenylphosphine (PPh_3), and aniline have been studied by ESCA. Their proposed structures have been confirmed using normalized ESCA intensities and binding energy shifts. No ESCA chemical shift was observed for the adduct between chloranil and HMB indicating that little charge had been transferred from the electron donor to the electron acceptor, i.e., the ground state of this adduct is essentially "nonbonding". When compared with the spectra of the unreacted species, a binding energy shift of approximately +2.0 eV for the N 1s peak was observed for the adduct between chloranil and TMPD. This shift was attributed to the presence of $TMPD^{2+}$ ions in the crystal lattice. The percentage of such ions in the adduct was determined to be 14.3%. Evidence for a phosphorus-oxygen bond in the chloranil-PPh_3 adduct was obtained by observing chemical shifts of the peaks arising from both O 1s and P 2p electrons. Two new adducts, chloranil-pyridine and chloranil-isoquinoline, were studied by ESCA. Structures are proposed for these adducts using information derived from their ESCA spectra.

I. Introduction

The structures of the products formed between chloranil (tetrachloro-*p*-benzoquinone) and tertiary phosphines or amines have been the topic of numerous reports.[1-8] However, the overall understanding of electron-transfer reactions in these systems is still not very satisfactory.[1] For instance, in the case of the adduct between chloranil and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), it is still questionable whether all ions in the crystal lattice are doubly charged. The exact percentage of the adduct molecules which are ionized has never been determined. Furthermore, no study has been reported on the adducts between chloranil and aromatic heterocycles.

X-Ray photoelectron spectroscopy (ESCA) is suitable for studying electron donor–acceptor systems because of its ability to elucidate the structure of a reaction product and to detect any redistribution of charge within the molecules resulting from charge transfer.[9] In the present work, a selected series of adducts between chloranil and hexamethylbenzene (HMB), TMPD, triphenylphosphine (PPh_3), and aniline has been examined by ESCA. In addition the interaction between chloranil and pyridine-type heterocycles has been investigated; the structures of the resulting adducts will be discussed.

II. Experimental Section

A. **Samples.** The adduct I of HMB and chloranil was prepared by adding a solution of freshly recrystallized chloranil (492 mg, 2 mmol) in 40 ml of anhydrous benzene to a solution of HMB (324 mg, 2 mmol) in 10 ml of anhydrous benzene under a nitrogen atmosphere. A purple color appeared immediately, together with a red-brown precipitate. After a total of 2 hr, the precipitate was filtered, washed with benzene, and dried in vacuo.

The adduct II of TMPD and chloranil was prepared as described by Pott and Kommandeur.[4]

The adduct III of PPh_3 and chloranil was prepared as described by Lucken et al.[7]

The adduct IV of aniline and chloranil was prepared as described by Nagakura et al.[8]

The adduct V of pyridine and chloranil was prepared by dissolving 492 mg (2 mmol) of freshly recrystallized chloranil in 50 ml of pyridine under a nitrogen atmosphere. A deep reddish brown color appeared almost immediately. A dark brown precipitate was forced out by adding a large quantity of anhydrous ether; the precipitate was filtered, washed with anhydrous ether, and dried in vacuo.

The adduct VI of isoquinoline and chloranil was prepared in exactly the same way as adduct V; a black precipitate was obtained.

B. Procedure. ESCA spectra were recorded with an AEI ES200 electron spectrometer using the Mg Kα line (1253.6 eV). The X-ray power supply was run at 12 kV and 20 mA. Pressure in the sample chamber during the scans was approximately 10^{-8} Torr.

The samples were examined by compressing powdered adducts onto copper mesh which was then mounted on the sample probe. To correct for charging effects and the spectrometer work function, spectra were recorded on samples which had evaporated onto their surfaces submonolayer amounts of crystalline gold. The gold $4f_{7/2}$ line was taken as 83.8 eV[10] and was used for calibration.

Adducts V and VI polymerized in the atmosphere within a few seconds. Therefore the entire sampling procedure was done in a drybox under nitrogen. The samples were mounted into a specially designed air-tight sample probe to allow transfer of the sample from the drybox into the spectrometer under an inert, moisture-free atmosphere.

Solid reagents such as chloranil, HMB, TMPD, and PPh_3 were run in the same way as adducts I to IV. Liquid reagents such as aniline, pyridine, and isoquinoline were examined by condensing them onto clean gold backings in situ. The liquids were injected into a heated reservoir shaft (~350°K), diffused as gases into the sample chamber, and condensed on the cooled sample probe (~180°K). The probe temperature, in each case, was carefully adjusted so that a steady state was established between evaporation and condensation. The gold reference substrate was always visible during the scans. The pressure remained at about 5×10^{-6} Torr in the sample chamber under these conditions.

Overlapping peaks were deconvoluted using a Du Pont 310 curve resolver. All spectra were run in triplicate and all peak positions are reported with a precision of ±0.2 eV.

The atomic ratios for adducts I to IV were calculated from their actual structures. Since the structures of adducts V and VI were unknown, the atomic ratios were obtained from elemental analyses. The formula found for adduct V is $C_{21}H_{15}N_3O_2Cl_4$ and for adduct VI it is $C_{33}H_{21}N_3O_2Cl_4$.

Peak areas were measured for a number of well-defined organic compounds for C 1s, N 1s, O 1s, Cl $2p_{3/2}$, and P 2p peaks; the relative ratios of these areas were 0.27, 0.40, 0.59, 0.64, and 0.31, respectively, normalized to the F 1s peak which was assigned a value of 1.00. Peak areas measured for each adduct were first normalized by dividing the experimental value by its corresponding intensity factor. The resulting numbers were then multiplied by a constant factor to give the normalized relative intensities listed in Table I. The multiplication, in effect, scaled the normalized relative intensities to approximate the actual atomic ratios. Normalized relative intensities are reported with a precision of ±5%.

Analysis of ionic chlorine for adducts V and VI was carried out by precipitating silver chloride from a methanol solution of the adduct. The results showed there are two chloride ions per molecule for both adduct V and adduct VI.

Table I. Binding Energies, Binding Energy Shifts, Normalized Relative Intensities, and Actual Atomic Ratios of the Various ESCA Peaks of the Adducts

Adduct	Peak[a]	Binding[b] energy, eV	Binding[c] energy shift, eV	Normalized[d] rel intensity	Actual[e] atomic ratio
(I) Chloranil–HMB	Cl $2p_{3/2}$	200.9	0.0	4.0	4
	O 1s	532.2	0.0	2.2	2
(II) Chloranil–TMPD	Cl $2p_{3/2}$	200.9	0.0	4.0	4
	O 1s (i)	531.8	−0.4	0.3	2
	(ii)	533.1	0.9	1.6	
	N 1s (i)	400.0	0.2	1.8	2
	(ii)	402.1	2.0	0.3	
(III) Chloranil–PPh_3	Cl $2p_{3/2}$	200.8	−0.1	4.0	4
	O 1s (i)	531.2	−1.0	1.1	1
	(ii)	534.0	1.8	1.0	1
	P 2p	132.9	1.9	1.0	1
(IV) Chloranil–aniline	Cl $2p_{3/2}$	200.8	−0.1	2.0	2
	O 1s	532.1	−0.1	2.1	2
	N 1s	400.3	0.6	2.1	2
(V) Chloranil–pyridine	Cl $2p_{3/2}$ (i)	200.9	0.0	2.0	2
	(ii)	198.0	−2.9	1.9	2
	O 1s (i)	531.2	−1.0	1.1	1
	(ii)	534.1	1.9	1.0	1
	N 1s	402.0	2.6	2.9	3
(VI) Chloranil–isoquinoline	Cl $2p_{3/2}$ (i)	200.9	0.0	2.0	2
	(ii)	198.0	−2.9	2.0	2
	O 1s (i)	531.2	−1.0	0.9	1
	(ii)	534.0	1.8	1.0	1
	N 1s	401.5	2.2	3.0	3

[a] C 1s peaks were not included in this table because the relatively large contamination signal at 285.0 eV makes deconvolution and the assignment of the various C 1s peaks very arbituary. [b] Relative to Au $4f_{7/2}$ peak taken as 83.8 eV. [c] Shifts in binding energies of the adducts relative to the unreacted molecules. [d] Normalized with respect to the ESCA atomic sensitivity. [e] From the formulas of the proposed structure.

III. Results and Discussion

The adducts studied are listed in Table I along with appropriate chemical shift and intensity data. Tabulated in the third and the fourth columns, respectively, are core electron binding energies and binding energy shifts relative to the unreacted molecules. While peak locations indicate the presence of elements such as C, O, N, P, and Cl in the adducts, binding energy shifts help to identify their respective oxidation states and/or partial atomic charges. Shifts in binding energies corresponding to different partial charges for these elements can be found in other reports.[9,11-13] However, correction for crystal potential effects are necessary to correlate ESCA chemical shifts with calculated charge.

Normalized relative intensities, as shown in Table I, are related to the number of such atoms per molecule present in the adduct. If a certain atom, such as the nitrogen in adduct II, exists with two different charges or oxidation states in the crystal, their relative atomic ratio is the ratio between their normalized relative intensities. The fact that all the normalized relative intensities, rounded to the nearest whole number, are equal to the actual atomic ratios for known adducts shows that such quantities can be very useful in using ESCA for semiquantitative analysis.

Adducts I-IV have been studied by other techniques, and their structures have been discussed.[1-8] Each of these adducts illustrates a different reaction pathway that may occur when chloranil is mixed with an electron donor in a suitable solvent. In reexamining adducts I-IV with ESCA, we have been able to answer certain questions concerning the exact percentage of ions in the adducts and have confirmed the proposed structures of these adducts. Thus one has the opportunity to evaluate ESCA for studying electron donor-acceptor systems. Adducts V and VI are new and their structures have not been reported. For these two adducts, we demonstrate how ESCA may be used to deduce structures.

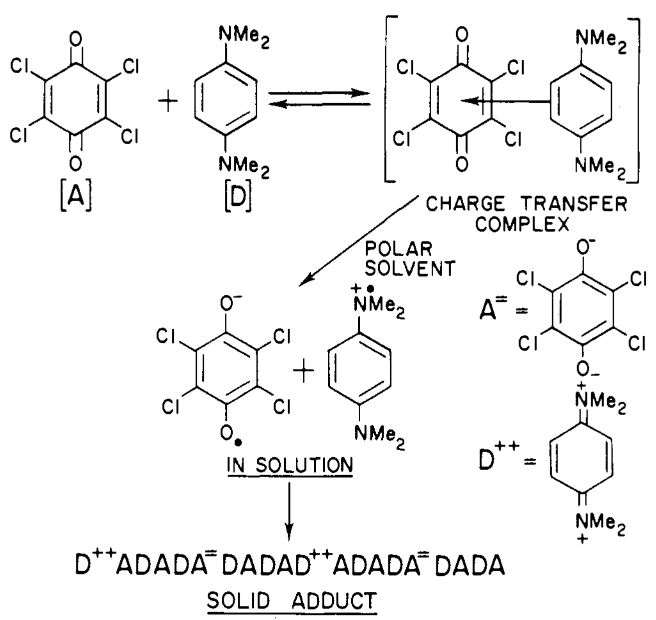


Figure 1. Formation of the charge-transfer complex between chloranil and TMPD.

Adduct I between chloranil and HMB is a typical example of a weak molecular complex with a well-defined crystal structure.[2] No binding energy shifts were observed for any of the peaks associated with adduct I as can be seen from Table I. In fact the ESCA spectra of this needle-shaped crystalline adduct are identical with the spectrum of a 1:1 powder mixture of the components. The absence of binding energy shifts points out the fact that the ground state of the chloranil-HMB complex is essentially "nonbonding", i.e., little charge is transferred from HMB to chloranil. This is not surprising since most complexes formed between a π electron donor and a π acceptor have nonbonding ground states.[1] The binding forces responsible for adduct stability are "physical" forces such as dipole-dipole or dipole induced-dipole interactions.

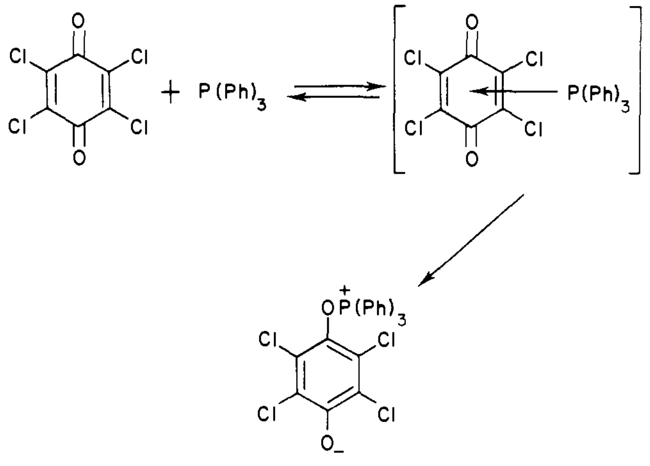
Adduct II between TMPD and chloranil is a typical example of a product from charge-transfer complexes involving relatively strong donors and strong acceptors. Actual transfer of charge from the donor to the acceptor has been detected in solution by ultraviolet absorption bands.[3] The accepted mechanism[1] for the formation of these ions in a suitable solvent is shown in Figure 1.

Pott and Kommandeur[4] suggested that in the crystal lattices, divalent ions are formed as a result of disproportionation of monovalent ions. A molionic lattice model has been proposed for this adduct in the solid state. According to this proposal, the crystal lattice of the complex is composed of chains of donors (D) and acceptors (A) ordered in the following way

$$D^{2+}\ ADADA^{2-}DADAD^{2+}\ ADADA^{2-}DADAD^{2+}\ ADADA^{2-}DADAD^{2+}\ ADADA^{2-}$$

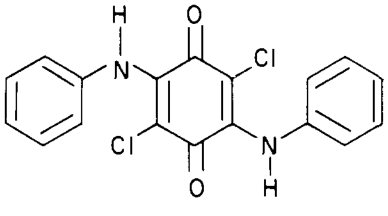
The above authors estimated that one out of every five donors (or acceptors) will be a divalent ion.[4]

In the ESCA spectrum of freshly prepared II, we observed two nitrogen peaks at binding energies of 400.0 and 402.1 eV with normalized relative intensities of 1.8 and 0.3,



ADDUCT (III)

Figure 2. Reaction mechanism for the formation of adduct III between chloranil and PPh$_3$.



ADDUCT (IV)

Figure 3. Structure of adduct IV of chloranil and aniline.

respectively (see Table I). The nitrogen at 402.1 eV binding energy corresponds to a nitrogen having a positive charge.[11] This means that 0.3 out of every 2.1 nitrogen atoms in the solid adduct is positively charged, i.e., one seventh or 14.3% of the nitrogens. Therefore if the molionic lattice model is correct, ESCA data suggest that one out of every seven donors or acceptors will be divalent. This result is different from that of Pott and Kommandeur.[4] However, their value was obtained through a calculation based entirely on estimating the contraction of the chains caused by the presence of divalent ions. The contraction of the chains was obtained from X-ray diffraction data. The values thus obtained are only approximations at best.

The oxygen data for adduct II indicate that 0.3 out of every 1.9 atoms of oxygen in the solid adduct is negatively charged. This gives a percentage of 15.8% which is in substantial agreement with the nitrogen data. However, more weight should be put on the nitrogen data because the N 1s peak is free from interference, while the O 1s peak may have some contribution from contaminants in the sample chamber. Thus, ESCA has been demonstrated to be a means of accurately measuring the concentration of divalent ions in the lattice. Electron spin resonance (ESR) has not been helpful because the divalent ions are not paramagnetic.

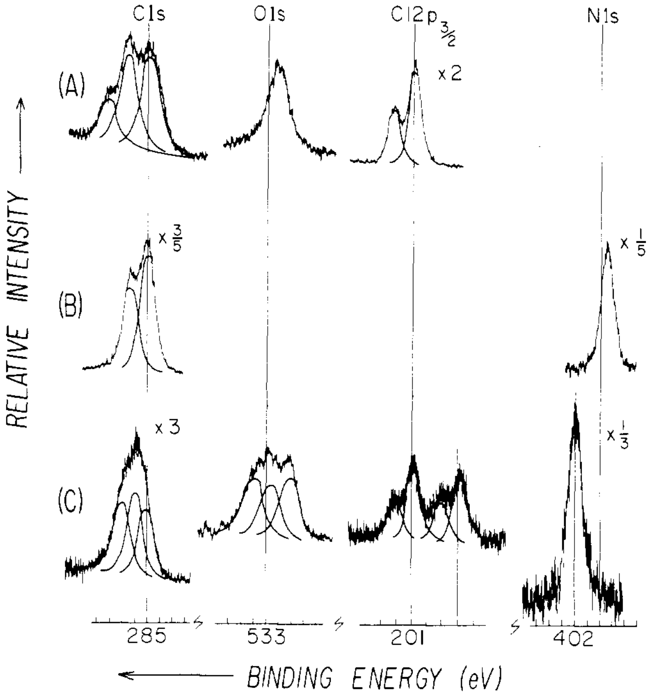


Figure 4. ESCA spectra showing photoelectron peak positions of: (A) chloranil, O 1s 532.2 eV, C 1s 286.5 and 288.1 eV, Cl 2p$_{3/2}$ 200.9 eV; (B) pyridine, N 1s 399.4 eV, C 1s 285.0 and 286.1 eV; and (C) adduct V of chloranil and pyridine, O 1s 531.2 and 534.1 eV, N 1s 402.0 eV, C 1s 285.0, 286.0, and 287.1 eV, Cl 2p$_{3/2}$ 200.9 and 198.0 eV. Contaminants in the sample chamber contribute peaks, e.g., peaks for samples A and C, at 285 and 532.6 eV.

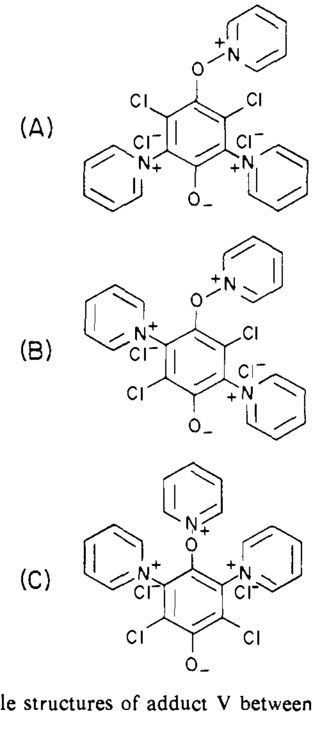


Figure 5. Possible structures of adduct V between chloranil and pyridine.

The interaction between chloranil and electron donors does not always produce a molecular complex. Sometimes the reaction proceeds further and new products result. For example, ESCA data for the adduct between chloranil and triphenylphosphine are consistent with a 1:1 addition product for III. A binding energy shift of 1.9 eV for phosphorus 2p electrons corresponds to a phosphinium type species.[12] A negligible shift of 0.1 eV for the chlorines indicates that substitution at chlorine sites is absent. Furthermore, of the two carbonyl oxygens, one is shifted positively and the other is shifted negatively. All this suggests strongly that the positively charged phosphorus atom is attached to one of the carbonyl oxygens in chloranil. Thus the ESCA data are consistent with the structure shown in Figure 2. The phenoxide-O-phosphonium dipolar ion structure for adduct III has previously been proposed by Ramirez et al.[6] Our ESCA data give further evidence for the existence of the phosphorus-oxygen bond between PPh$_3$ and chloranil.

The interaction between aniline and chloranil is different from that between PPh_3 and chloranil. Normalized relative ESCA intensities for adduct IV indicate that there are only two chlorine atoms per molecule, and two nitrogens per molecule for the adduct. Furthermore, both chlorine and oxygen peaks of the adduct are essentially unshifted from those of the component molecules indicating that two chlorines may have been substituted by two anilines. The ESCA data are in good agreement with the proposed structure of 2,5-dichloro-3,6-dianilino-*p*-benzoquinone by Nagakura et al.[8] (see Figure 3). However, one should notice that ESCA data do not provide information concerning the chlorine positions at which substitution occurs, i.e., a 2,3 adduct would give the same spectrum as adduct IV.

The interaction between chloranil and pyridine to give adduct V seems to be rather complicated. Normalized relative intensity measurements suggest that adduct V is formed between three molecules of pyridine and one molecule of chloranil. Results from elemental analysis gave an empirical formula of $C_{21}H_{15}N_3O_2Cl_4$ for adduct V, exactly that of a 3:1 adduct of pyridine and chloranil.

Assuming that V is a 3:1 adduct of pyridine and chloranil, the possible structures of adduct V can be deduced by making the following observations. (1) Only a single nitrogen peak at a binding energy of 402.0 eV was observed in the ESCA spectrum of the adduct (see Figure 4). This shift of +2.6 eV from pyridine corresponds to the nitrogens found in pyridinium ions.[11] Thus, all three pyridines must link to chloranil through the nitrogen atoms. (2) There are two Cl 2p peaks of equal intensities in the spectrum of adduct V. One of these Cl 2p peaks has a chemical shift of −2.9 eV, indicating that two of the four chlorines are ionic. This suggests that two chlorines have been replaced by two pyridinium ions to give two chloride ions. The existence of two chloride ions per molecule has been confirmed by wet chemical analysis. (3) The oxygens of adduct V have essentially the same binding energies as the two oxygens in adduct III. These observations lead to the conclusion that in adduct V two of the pyridinium ions have replaced two of the chlorines on the ring and the third pyridinium ion is attached to one of the carbonyl oxygens.

The question concerning which chlorine positions have been attacked cannot be answered without further information such as the initial position of attack by pyridine. However, substitution at two adjacent chlorines would be greatly hindered by steric effects and such structures can probably be neglected. Even so, three structures for adduct V remain possible and these are shown in Figure 5. Molecular models were employed in an attempt to predict the most probable structure among the three; structure A of Figure 5 seems to be more likely because it has the least steric hindrance.

Normalized relative intensities of adduct VI are in good agreement with formation of a 3:1 adduct between isoquinoline and chloranil, analogous to the pyridine adduct. Elemental analysis gave an empirical formula of $C_{33}H_{21}N_3O_2Cl_4$, which corresponds to three molecules of isoquinoline and one molecule of chloranil. Binding energy shifts for Cl $2p_{3/2}$, O 1s, and N 1s peaks are similar to those of adduct V. Wet chemical analysis of ionic chlorine for adduct VI shows that there are two chloride ions for each molecule. In view of all these observations, structures similar to those in Figure 5 with pyridinium ions replaced by isoquinolinium ions are proposed for the adduct between chloranil and isoquinoline.

IV. Conclusion

The use of normalized relative intensity measurements for semiquantitative analysis by ESCA has proved to be successful. ESCA is shown capable of detecting a small amount of ions present in a predominantly molecular lattice. The potential of using ESCA to aid in elucidating structures of molecular solids has also been demonstrated. Combining all these advantages, ESCA should prove to be a powerful tool for the study of electron donor-acceptor systems.

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